

## (19) World Intellectual Property Organization International Bureau





## (43) International Publication Date 27 June 2002 (27.06.2002)

### **PCT**

# (10) International Publication Number WO 02/50161 A2

(51) International Patent Classification7:

\_\_\_\_

C08G 65/00

(21) International Application Number: PCT/US01/48353

(22) International Filing Date:

12 December 2001 (12.12.2001)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

09/742,974

20 December 2000 (20.12.2000) US

(71) Applicant: BAYER CORPORATION [US/US]; 100 Bayer Road, Pittsburgh, PA 15205-9741 (US).

(72) Inventors: SCHILLING, Steven, L.; 250 Lynn Haven Drive, Pittsburgh, PA 15228 (US). DOERGE, Herman, P.; 9332 Timber Trail, Pittsburg, PA 15237 (US). BALL, Edward, E.; 200 Beacon Drive Ext., Weirton, WV 26062 (US). HEADLEY, Keith, J.; 609 South 2nd Avenue, Paden City, WV 26159 (US).

(74) Agents: WHALEN, Lyndanne, M. et al.; 100 Bayer Road, Pittsburgh, PA 15205-9741 (US).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

#### Published:

 without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

/50161 A

(54) Title: CO-INITIATED POLYOLS USEFUL FOR THE PRODUCTION OF RIGID POLYURETHANE FOAMS

(57) Abstract: A co-initiated polyether polyol is produced by suspending a solid polyhydroxyl compound in an amine-initiated polyol, heating the suspension and alkoxylating the heated suspension. These co-initiated polyether polyols are particularly useful for the production of polyurethanes.

# CO-INITIATED POLYOLS USEFUL FOR THE PRODUCTION OF RIGID POLYURETHANE FOAMS

5

10

15

20

25

30

### BACKGROUND OF THE INVENTION

The present invention relates to co-initiated polyether polyols useful for the production of rigid polyurethane foams and to a process for the production of such co-initiated polyols.

Processes for the production of polyether polyols from materials which are normally solid at ambient conditions such as sucrose are known. In many of the known processes, the solid material is dissolved or suspended in a solvent prior to reaction with the selected alkylene oxide(s) to facilitate processing of the reaction mixture. The solvent can either be an inert material such that disclosed in U.S. Patent 3,941,769 or a reactive material such as water (U.S. Patent 5,596,059).

The presence of water or an inert organic solvent during the reaction of the solid material with the alkylene oxide, however, is undesirable for a number of reasons. First, the solvent takes up space in the reactor which might otherwise be used to produce larger batches of polyol. Second, the solvent or unreacted water must be removed, usually by distillation. Such removal consumes both time and energy. Finally, if water is used to suspend or dissolve the sucrose, difunctional glycols which reduce the average functionality of the polyol produced are formed. One proposed solution to this problem is removal of the solvent by distillation after a portion of the alkylene oxide has been added. (See, e.g., U.S. Patent 3,085,085 which discloses removal of water by distillation.) Such removal of water after adding and reacting a portion of the total alkylene oxide desired reduces the amount of glycols formed and allows for a larger batch size but still consumes time and energy.

In commercial processes for the production of polyurethane foams, mixtures or blends of individual polyols are generally used as the polyol

10

15

20

25

30

component to be reacted with the isocyanate component. Use of such mixtures makes it possible to produce polymers having specific physical properties suited for a particular application.

When developing new systems, combination of individual polyols makes it easier to optimize a system for the production of polymers having a desired combination of properties. However, once a system has been optimized, the flexibility achieved by use of individual polyols is no longer necessary. This is particularly true where one or more of the polyols in the optimized system is difficult to manufacture such as polyols based on solid initiators such as sucrose. In such cases, it may be desirable to produce a co-initiated polyol which duplicates the properties obtained from the blend of individual polyols.

In U.S. Patent 5,684,057, for example, a polyol composition to produce a rigid foam having improved thermal insulation and dimensional stability when specified blowing agents were used was sought. The polyol composition developed includes at least three different types of polyol. The polyol composition required in this patented process includes: (1) an aromatic amine-initiated polyether polyol, (2) an aliphatic amine-initiated polyether polyol, and (3) a polyester polyol. This patent teaches that the individual polyols may be combined prior to reaction with the polyisocyanate. It is preferred, however, that the aromatic amine-initiated and aliphatic amine-initiated polyols be prepared by a co-initiation process in which the aliphatic and aromatic amine initiators are first blended together and the resultant blend is subsequently alkoxylated. The required polyester polyol is then added to the propoxylated blend.

U.S. Patent 5,596,059 discloses polyol blends for the production of flexible foams which do not require the use of expensive initiators such as glycerine or of solvents such as toluene. These polyol blends are prepared by alkoxylating aqueous solutions of one or more solid, polyhydric, hydroxy-functional initiators to produce a blend of low functionality diols and higher functionality polyols. A key feature of this process, is the alkoxylation of the water used as solvent. This alkoxylation

of water eliminates the need for water removal and the need to use expensive conventional initiators such as glycerine or solvents. Water coinitiated polyols such as these, however, are not useful for the production of rigid polyurethane foams because of their low functionalities and hydroxyl numbers.

A polyol blend for the production of rigid polyurethane foams which could be prepared from a solid polyhydroxyl compound initiator by a simple process without the need to use a solvent would, therefore, be advantageous.

## 10 <u>SUMMARY OF THE INVENTION</u>

5

15

20

25

30

It is an object of the present invention to provide a process for the production of a co-initiated polyether polyol from a polyhydroxyl compound that is normally solid at processing conditions without the need to use large quantities of a solvent that must be removed prior to use of that co-initiated polyol and without generating large amounts of low functionality diols.

It is also an object of the present invention to provide a more efficient and economical process for the production of a co-initiated polyether polyol having a functionality of at least 4 from a polyhydroxyl compound that is normally solid at processing conditions.

It is a further object of the present invention to provide a co-initiated polyol for the production of rigid polyurethane foams which produces foams having properties comparable to foams made with polyols formed by the conventional method for producing blends, i.e., combining individual polyols.

These and other objects which will be apparent to those skilled in the art are accomplished by suspending a solid polyhydroxyl initiator having a functionality of at least 4 and a melting or decomposition point above 95°C in an amine-initiated polyol, heating the suspension, (preferably, in the presence of an alkaline catalyst) and alkoxylating the resultant mixture. The alkaline catalyst may then be neutralized and/or

10

15

20

25

30

removed from the alkoxylated mixture. The alkoxylation product may then be used in a process for the production of rigid polyurethane foams.

### DETAILED DESCRIPTION OF THE PRESENT INVENTION

The present invention relates to a new method for producing co-initiated polyether polyols from polyhydroxyl compounds that are solids at ambient temperature without the use of an inert solvent such as toluene or the large quantities of water necessary to suspend or dissolve the solid polyhydroxy compound. In this method, at least one solid polyhydroxyl compound is suspended in at least one amine-initiated polyol, the suspension is heated to or maintained at a temperature of at least 80°C in the presence of an alkaline catalyst and subsequently alkoxylated. The alkaline catalyst is then neutralized and/or removed from the alkoxylated mixture by any of the known techniques such as neutralization with sulfuric acid or lactic acid, extraction or decantation. The resultant alkoxylated mixture may then be used to prepare rigid polyurethane foams.

The solid polyhydroxyl compounds useful as the initiator to be suspended in the amine-initiated polyol have a hydroxyl group functionality of at least 4 and melt at temperatures above 95°C or decompose before melting. Examples of suitable polyhydroxyl compound initiators include: pentaerythritol, dipentaerythritol, glucose, sorbitol, lactose, mannitol, fructose, sucrose, hydrolyzed starches, saccharide and polysaccharide derivatives such as alpha-methylglucoside and alpha-hydroxyethylglucoside. Sorbitol, sucrose, and pentaerythritol are particularly preferred.

The amine-initiated polyol in which the solid polyhydroxyl compound is suspended may be any of the known amine-initiated polyether polyols which is liquid at temperatures of from about 70 to about 150°C, has a viscosity at the processing temperature which is sufficiently low that it will form a suspension that can be stirred, and has a hydroxyl number sufficiently high that upon alkoxylation the co-initiated polyether polyol product will have the predetermined hydroxyl number of greater than 300 mg KOH/g. The hydroxyl number of the amine-initiated polyols will generally be at least 500, preferably at least 550, most preferably at least

-5-

600 mg KOH/g. The hydroxyl numbers given herein are determined in accordance with ASTM D-2849-69, Method C.

5

10

15

20

25

30

Examples of suitable amines that may be used to prepare the amine-initiated polyether polyols satisfying these criteria include: 2,4'-, 2,2'-, and 4,4'-methylene dianiline; 2,6- or 2,4-toluene diamine and vicinal toluene diamines; p-aminoaniline; 1,5-diaminonaphthalene; mixtures of methylene dianiline and its higher homologs; ethylene diamine, propylene diamine; diethylene triamine; 1,3-diaminopropane; 1,3-diaminobutane; and 1,4-diaminobutane. Ethylene diamine and toluene diamines are particularly preferred. Ammonia and aminoalcohols which can be prepared by the alkoxylation of ammonia are not included among the amine-initiators to be used in the amine-initiated polyols required for the practice of the present invention.

The amine-initiated polyols may be produced by any of the known methods. Generally, such polyols are produced by alkoxylating the amine initiator, either with or without an alkaline catalyst, until the desired hydroxyl number has been attained.

Suitable alkoxylating agents include any of the known alkylene oxides such as ethylene oxide, propylene oxide, butylene oxide, amylene oxide, and mixtures thereof. Ethylene oxide and propylene oxide are preferred.

In accordance with the present invention, the solid polyhydroxyl compound initiator is added to the liquid amine-initiated polyol and stirred, mixed or agitated sufficiently to disperse the polyhydroxyl compound initiator in the amine-initiated polyol and form a solution or a suspension. The amine-initiated polyol is generally used in an amount that is at least 30% by weight (based on the weight of the solid polyhydroxyl compound), preferably at least 40% by weight, most preferably, at least 50% by weight.

The addition of solid polyhydroxyl compound to the amine-initiated polyol is generally carried out at a temperature less than 120°, preferably from about 70 to about 110°C, most preferably from about 80 to about 100°C.

10

15

20

25

30

 $\langle \cdot \rangle$ 

3

In addition to the solid polyhydroxyl compound, other starting materials commonly used in the production of polyether polyols and any of the catalysts commonly used to produce polyether polyols may, optionally, also be included in the suspension. Examples of other starting materials that may optionally be included in the suspension are small quantities of water, ethylene glycol, propylene glycol and glycerine. As used herein, "small quantities of water" means less than about 10% by weight, based on the weight of the solid polyhydroxyl compound initiator, including water added with any aqueous catalyst solution. The total quantity of these other, optional, starting materials should not, however, be greater than 25% by weight, based on the weight of the solid polyhydroxyl compound initiator.

Examples of catalysts that may be included in the suspension include potassium hydroxide and sodium hydroxide. When sucrose is used as the solid polyhydroxyl compound initiator, an alkaline catalyst such a potassium hydroxide should be included in the solution or suspension.

After the suspension of the solid polyhydroxyl compound in the amine-initiated polyol has been formed, the suspension is adjusted to a temperature of from about 80 to about 150°C, preferably from about 90 to about 140°C, most preferably from about 100 to about 130°C. This heated suspension is then alkoxylated in accordance with any of the procedures known to those skilled in the art using an alkylene oxide such as ethylene oxide and/or propylene oxide at a temperature of from about 80 to about 150°C, preferably from about 90 to about 140°C, most preferably from about 100 to about 130°C. This alkoxylation is carried out until the desired hydroxyl number is attained. The co-initiated polyol of the present invention will generally have a hydroxyl number of from about 300 to about 600, preferably from about 350 to about 550, most preferably from about 400 to about 500 mg KOH/g, and a number average functionality of from about 4 to about 6, preferably from about 4 to about 5.

-7-

However, it is also possible to produce a co-initiated polyether polyol having a lower or a higher hydroxyl number by simply increasing or decreasing the amount of alkoxylation agent added. It is also possible to produce a co-initiated polyether polyol having a higher or lower functionality by selecting an amine-initiated polyol having a different functionality or by varying the ratio of amine polyol to solid polyhydroxyl compound to any other starter material used.

5

10

15

20

25

30

A key feature of the present invention is the ability to produce a polyether polyol from a solid polyhydroxyl compound without the use of added solvent and without sacrificing any of the product properties. The absence of a solvent makes it possible to produce the desired co-initiated polyether polyol in greater quantity without increasing the volume of the reaction vessel. Further, the production cycle time is reduced because there is no need for the additional processing step of solvent removal. Finally, safety, health and environmental concerns encountered with use of solvents such as flammability, toxicity, and environmental releases are avoided.

After any alkaline catalyst present has been neutralized and/or removed, the co-initiated polyether polyols produced in accordance with the present invention may be used for the production of rigid polyurethane foams in accordance with known methods. These co-initiated polyether polyols may be used alone or in combination with other polyols.

Other polyols which may optionally be used in combination with the co-initiated polyether polyols of the present invention include polyether polyols prepared from liquid polyhydroxyl compounds, polyether polyols prepared from polyhydroxyl compounds having functionalities of less than 4, polyether polyols prepared from ammonia or aminoalcohols, polyester polyols and combinations thereof.

The additives and processing aids typically included in the polyol component of a foam-forming mixture may, of course, be added to the co-initiated polyether polyols of the present invention prior to use of the co-initiated polyether polyol to produce a rigid polyurethane foam. Examples

of such suitable additives and processing aids include: catalysts, blowing agents, water, chain extenders, crosslinking agents, surfactants, foam stabilizers, cell regulators, fillers, dyes, pigments, flame retardants, hydrolysis protection agents, fungicides and bacteriocides.

5

10

Suitable catalysts include organometallic, preferably organotin catalysts, and tertiary amine catalysts. Examples of suitable tin catalysts are tin (II) acetate, tin (II) octanoate, tin (II) laurate, dialkyl tin diacetates, and dibutyl tin dichloride. Examples of suitable tertiary amine catalysts include: N,N-dimethyl cyclohexyl amine, pentamethyl diethylene triamine, and N, N', N"-tris(3-dimethyl aminopropyl)hexahydro-S-triazine. Tertiary amines are the preferred catalysts.

Suitable blowing agents include any of those known in the art used

15

(6)

singly or in combination. Hydrocarbons, hydrofluorocarbons (HFCs), and hydrochlorofluorocarbons (HCFCs) and carbon dioxide generated from the reaction of water with an isocyanate are particularly suitable. Specific examples of suitable blowing agents are: 1,1-dichloro-1-fluoroethane (HCFC 141b), 1,1,1,2-tetrafluoro-ethane (HFC 134a), chlorodifluoromethane (HCFC 22), 1-chloro-1,1-difluoroethane (HCFC 142b), 1-chloro-1,2,2,2-tetrafluoroethane (HCFC 124), 1,1,2,2-

20

tetrafluoroethane (HFC 134), 1,1,1,3,3-pentafluoropropane (HFC 245fa), 1,1,1,3,3-pentafluorobutane (HFC 365mfc), 1,1,1,4,4,4-hexafluorobutane (HFC 356mffm), cyclopentane, isopentane, cyclo-hexane, and isobutane. Hydrocarbons and HFC's are the most preferred blowing agents because they have a zero ozone depletion potential.

25

30

The isocyanates which may be reacted with the co-initiated polyols of the present invention include any of the known aliphatic isocyanates, aromatic isocyanates, modified isocyanates, and isocyanate-terminated prepolymers. The isocyanate will generally have at least two isocyanate groups, preferably from 2 to 3 isocyanate groups per molecule. Examples of suitable isocyanates are: toluene diisocyanate (TDI), prepolymers of toluene diisocyanate, methylene diphenyl diisocyanate (MDI), prepolymers of methylene diphenyl diisocyanate, polymeric methylene diphenyl

10

15

diisocyanate (PMDI), and prepolymers of polymeric methylene diphenyl diisocyanate.

-9-

The isocyanate and the isocyanate-reactive component in which the co-initiated polyols of the present invention are present are generally reacted in amounts such the ratio of NCO to OH groups is from about 0.9 to about 3.0, preferably from about 1.0 to about 2.0, most preferably from about 1.05 to about 1.5.

Polyurethane foams made from the co-initiated polyether polyols of the present invention are characterized by physical properties comparable to those of foams made using mixtures of individual polyether polyols having the same amine and the same polyhydroxyl compound initiators and the same average hydroxyl numbers despite their inherent structural differences.

Having thus described our invention, the following Examples are given as being illustrative thereof. All parts and percentages given in these Examples are parts by weight and percentages by weight, unless otherwise indicated.

#### **EXAMPLES**

The materials used in the Examples were as follows:

- 20 POLYOL A: A polyether polyol prepared by propoxylating ethylene diamine having a hydroxyl number of about 770 mg KOH/g and a functionality of about 4 which is commercially available from Bayer Corporation under the designation Multranol 9181.
- 25 POLYOL B: A polyether polyol prepared by alkoxylating a sucrose, propylene glycol and water starter having a hydroxyl number of about 470 mg KOH/g and a functionality of about 5.2 which is commercially available from Bayer Corporation under the designation Multranol 9196.
- 30 POLYOL C: An aromatic amine-initiated polyether polyol having a hydroxyl number of about 395 mg KOH/g and a functionality

-10-

of about 4 which is commercially available from Bayer Corporation under the designation Multranol 8114.

- POLYOL D: An aromatic polyester polyol blend having a hydroxyl number of about 240 mg KOH/g and a functionality of about 2.0 which is commercially available from Stepan Company under the designation Stepanpol PS 2502A.
- ISOCYANATE A: A modified polymethylene polyphenyl polyisocyanate prepolymer having an NCO content of about 28.0% which is commercially available from Bayer Corporation under the designation Mondur E-577.
- SURFACTANT: A silicone-based surfactant that is commercially available from Air Products and Chemicals, Inc. under the designation Dabco DC 5357.
- CATALYST A: N, N', N"-tris(3-dimethylaminopropyl)-hexahydro-Striazine which is commercially available from Air Products under the designation Polycat 41.
  - CATALYST B: Pentamethyldiethylenetriamine which is commercially available from Rhein Chemie under the name Desmorapid PV.
- 20 HCFC 141b: 1,1-dichloro-1-fluoroethane.

#### Example 1

5

10

25

30

 $(\cdot,\cdot)$ 

2502 g of POLYOL A were charged to a 5 gallon reactor along with 718 g of propylene glycol, 112 g of water, 288 g of 46% KOH and 4579 g of sucrose. The contents of the reactor were then agitated and heated to about 110°C. 3040 g of ethylene oxide were then added to the reactor over a period of 190 minutes while maintaining the temperature at about 110°C and the pressure in the reactor below 30 psig. After addition of the ethylene oxide was completed, the contents of the reactor were allowed to react for a period of 60 minutes before the addition of propylene oxide was begun.

6450 g of propylene oxide were then added to the reactor which was maintained at a temperature of about 110°C and at a pressure below 30 psig.

After addition of the propylene oxide had been completed, the contents of the reactor were allowed to react for 3 hours. After the 3 hour reaction time, sufficient lactic acid was added to the reactor contents to neutralize the KOH catalyst. Water was removed from the reaction mixture by distillation and the contents of the reactor were then removed and analyzed.

The properties of the resultant co-initiated polyether polyol, of the individual polyether polyols POLYOLS A and B (prepared from the same initiators and the same relative amount of ethylene oxide and propylene oxide), and of a blend of POLYOLS A and B in which the ratio of A:B was 1:6.2 are summarized in Table 1.

15 <u>TABLE 1</u>

Property	POLYOL A	POLYOL B	1:6.2 BLEND	CO- INITIATED POLYOL
OH Number (mg KOH/g)	770	470	512 (calculated)	510
Viscosity (mPa·s at 25°F)	36,000	24,000		28,430
% Water	≤ 0.10	≤ 0.10	≤ 0.10	0.086

### Example 2

20

WO 02/50161

5

10

1440 g of ortho-toluene diamine (o-TDA) were charged to a reactor and heated to about 115°C. 1799 g of ethylene oxide were then added to the reactor and allowed to fully react with the o-TDA over a period of 60 minutes to form the amine-initiated polyether polyol. The contents of the reactor were then cooled to 90°C. 3739 grams of sugar, 586 grams of propylene glycol, 99.1 g of water, and 202.5 g of 46% potassium hydroxide

-12-

were then added to the reactor. The temperature of the reactor contents was then raised back to about 115°C and an additional 2483 g of ethylene oxide were added and allowed to react for one hour. 8616 g of propylene oxide were then added to the reactor. After allowing the propylene oxide to react for 3 hours, the contents of the reactor were neutralized with lactic acid and water was removed by distillation. The contents of the reactor were then removed and analyzed.

The results of this analysis of the co-initiated polyether polyol, of the corresponding individual polyether polyols and of a blend of the individual polyether polyols in which the ratio of POLYOL B to POLYOL C is 2:1 are reported in Table 2.

TABLE 2

PROPERTY	POLYOL B	POLYOL C	2:1 BLEND OF B:C	CO- INITIATED POLYOL
Hydroxyl Number (mg KOH/g)	470	390	443 (calculated)	454
Viscosity (mPa·s at 25°F)	24,000	9,000		18,277
% Water	≤ 0.10	≤ 0.10	≤ 0.10	0.028

5

10

## Example 3

The materials listed in Table 3 were combined in the amounts indicated in the Table and reacted with the amount of ISOCYANATE A indicated in the Table to produce a rigid polyurethane foam. The properties of the resultant foams are also reported in Table 3.

TABLE 3

Material or Property	SAMPLE A	SAMPLE B (COMPARATIVE)
Co-initiated polyol of	48.46	_
Example 1 (parts by wt.)		
POLYOL A (parts by wt.)		6.73
POLYOL B (parts by wt.)	-	41.73
POLYOL D (parts by wt.)	18.84	18.84
SURFACTANT (parts by	2.26	2.26
wt.)		
CATALYST A (parts by	0.44	0.44
wt.)		
CATALYST B (parts by	0.89	0.89
wt.)		
Water (parts by wt.)	1.20	1.20
HCFC 141b (parts by wt.)	27.91	27.91
ISOCYANATE A (parts	135.80	135.80
by wt.)		·
Cream Time (sec)	10	10
Gel Time (sec)	44	45
Shrinkage	None	None
Minimum Fill Density (lb/ft <sup>3</sup> )	1.77	1.75
Molded Panel Density (lb/ft³)	1.92	, 1.94
% Thickness Increase	1.0	1.0
after Demold		
Initial k-factor (Btu-in./hr	0.118	0.118
ft. <sup>2</sup> -°F) @ 75°F		
1 Month k-factor (Btu-	0.133	0.133
in./hrft. <sup>2</sup> -°F) @ 75°F		
3 Month k-factor (Btu- in./hrft.²-°F) @ 75°F	0.145	0.146

## Example 4

5

The materials listed in Table 4 were combined in the amount indicated in the Table and reacted with POLYISOCYANATE A in the amount indicated in the Table to produce a rigid polyurethane foam. The properties of the foams produced are also reported in Table 4.

TABLE 4

Material or Property	SAMPLE C	SAMPLE D
, }		(COMPARATIVE)
POLYOL from Example 2	53.31	
(parts by wt.)		
POLYOL B (parts by wt.)		35.52
POLYOL C (parts by wt.)		17.79
POLYOL D (parts by wt.)	14.84	14.84
SURFACTANT (parts by	2.38	2.38
wt.)		
CATALYST A (parts by	0.46	0.46
wt.)		
CATALYST B (parts by	0.92	0.92
wt.)		
Water (parts by wt.)	1.19	1.19
HCFC 141b (parts by wt.)	26.90	26.90
ISOCYANATE A (parts	121.02	121.02
by wt.)		
Cream Time (sec)	9	9
Gel Time (sec)	40	41
Friability	None	None
Minimum Fill Density	1.68	1.69
(lb/ft <sup>3</sup> )		
Molded Panel Density	1.94	1.92
(lb/ft <sup>3</sup> )		
Core Density (lb/ft³)	1.63	1.64
Initial k-factor (Btu-in./hr	0.120	0.119
ft. <sup>2</sup> -°F) at 35°F		
Initial k-factor (Btu-in./hr	0.126	0.127
ft.²-°F) at 75°F		
Perpendicular	12.5	14.7
Compression Strength		
(lbs/in²) @ 10%		
compression		
Closed Cell Content (%)	84.8	84.4

-15-

As these Examples illustrate, the co-initiated polyols of the present invention produce rigid polyurethane foams having substantially the same physical properties as foams produced from mixtures of individual polyols which the co-initiated polyols of the present invention are intended to replace. This substantial equivalence could not have been expected because the epoxide sequences and the hydroxyl numbers of the co-initiated polyols of the present invention are obviously different from those of individual polyether polyols used in the comparable polyol blends.

5

10

Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that variations can be made therein without departing from the spirit and scope of the invention except as it may be limited by the claims.

PCT/US01/48353

## WHAT IS CLAIMED IS:

1. A process for the production of a co-initiated polyether polyol comprising:

a) suspending

5

(1) a polyhydroxyl compound which melts above 95°C or decomposes before melting and has a hydroxyl group functionality greater than or equal to 4,

in

(2) an amine-initiated polyether polyol which

10

(i) is a liquid,

10

 (ii) has a viscosity sufficiently low that stirring of the amine-initiated polyol, the polyhydroxyl compound (1) and any optional materials present is possible at processing conditions,

15

(iii) has a hydroxyl number sufficiently high to permit reaction with enough ethylene oxide and/or propylene oxide to produce a co-initiated polyol having a selected hydroxyl number, and

20

( iv ) has a hydroxyl functionality greater than or equal to 4

in an amount such that a stirrable slurry or suspension is formed, and optionally,

(3) a catalyst, and

25

- (4) a co-initiator which is different from (1) or (2),
- b) heating the slurry or suspension generated in step a) to or maintaining the slurry at a temperature of from about 80 to about 150°C, and

30

c) reacting the heated slurry or suspension from step b) with ethylene oxide and/or propylene oxide to form the co-initiated polyol.

PCT/US01/48353

Control was a service of

5

10

20

25

- 2. The process of Claim 1 in which any catalyst present in the product of step c) is neutralized and/or removed.
- 3. The process of Claim 1 in which polyhydroxyl compound (1) is selected from the group consisting of sucrose, sorbitol and pentaerythritol.
- 4. The process of Claim 1 in which an alkaline catalyst is added to or incorporated into the suspension formed in step a).
- 5. The process of Claim 1 in which the amine-initiated polyether polyol (2) is selected from the group consisting of ethylene diamine-initiated and toluene diamine-initiated polyether polyols.
- 6. The process of Claim 1 in which no inert organic solvent is used.
- 7. The process of Claim 1 in which step a) is carried out at a temperature of from about 80 to about 100 °C.
- 15 8. The process of Claim 1 in which step b) is carried out at a temperature of from about 100 to about 130°C.
  - 9. The process of Claim 1 in which at least 30% by weight (based on the weight of polyhydroxyl compound (1)) of the amine-initiated polyol (2) is used.
    - 10. The co-initiated polyol produced by the process of Claim 1.
    - 11. The co-initiated polyol produced by the process of Claim 3.
  - 12. A process for the production of a rigid polyurethane foam comprising reacting the co-initiated polyol of Claim 10 with an isocyanate.
  - 13. A process for the production of a rigid polyurethane foam comprising reacting the co-initiated polyol of Claim 11 with an isocyanate.
    - 14. The rigid polyurethane foam produced by the process of Claim 12.
  - 15. The rigid polyurethane foam produced by the process of Claim 13.

## (19) World Intellectual Property Organization International Bureau





## (43) International Publication Date 27 June 2002 (27.06.2002)

## **PCT**

## (10) International Publication Number WO 02/050161 A3

(51) International Patent Classification<sup>7</sup>: 18/48, 65/26

C08G 18/50,

(21) International Application Number: PCT/US01/48353

(22) International Filing Date:

12 December 2001 (12.12.2001)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

09/742,974

20 December 2000 (20.12.2000) U

(71) Applicant: BAYER CORPORATION [US/US]; 100
Bayer Road, Pittsburgh, PA 15205-9741 (US).

(72) Inventors: SCHILLING, Steven, L.; 250 Lynn Haven Drive, Pittsburgh, PA 15228 (US). DOERGE, Herman, P.; 9332 Timber Trail, Pittsburg, PA 15237 (US). BALL, Edward, E.; 200 Beacon Drive Ext., Weirton, WV 26062 (US). HEADLEY, Keith, J.; 609 South 2nd Avenue, Paden City, WV 26159 (US).

(74) Agents: WHALEN, Lyndanne, M. et al.; 100 Bayer Road, Pittsburgh, PA 15205-9741 (US).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

#### Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments
- (88) Date of publication of the international search report: 22 August 2002

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

050161 A3

(54) Title: CO-INITIATED POLYOLS USEFUL FOR THE PRODUCTION OF RIGID POLYURETHANE FOAMS

(57) Abstract: A co-initiated polyether polyol is produced by suspending a solid polyhydroxyl compound in an amine-initiated polyol, heating the suspension and alkoxylating the heated suspension. These co-initiated polyether polyols are particularly useful for the production of polyurethanes.

### INTERNATIONAL SEARCH REPORT

Inte al Application No PCT/US 01/48353

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C08G18/50 C08G C08G65/26 C08G18/48 According to International Patent Classification (IPC) or to both national classification and IPC B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C08G Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data C. DOCUMENTS CONSIDERED TO BE RELEVANT Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No. 1-15 US 3 640 997 A (FIJAL WALTER R) X 8 February 1972 (1972-02-08) claims 1-3 column 3, line 9-13 column 4, line 14-16 column 2, line 49-51 examples 1-16 10-15 US 5 030 758 A (DIETRICH MANFRED ET AL) X 9 July 1991 (1991-07-09) claim 1 column 3, line 52-59 examples 1-19 Patent family members are listed in annex. Further documents are listed in the continuation of box C. Special categories of cited documents: "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international "X" document of particular relevance; the claimed invention filing date cannot be considered novel or cannot be considered to "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such docudocument referring to an oral disclosure, use, exhibition or other means ments, such combination being obvious to a person skilled in the art. document published prior to the international filing date but later than the priority date claimed \*&\* document member of the same patent family Date of mailing of the international search report Date of the actual completion of the international search 01/07/2002 25 June 2002 Authorized officer Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040. Tx. 31 651 epo nl, Fax: (+31-70) 340-3016 Kositza, M

## INTERNATIONAL SEARCH REPORT

In mail Application No PCT/US 01/48353

ategory °	tion) DOCUMENTS CONSIDERED TO BE RELEVANT  Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
(	US 3 941 769 A (MAASSEN DIETER ET AL) 2 March 1976 (1976-03-02) claim 1 column 3, line 50-66 column 5, line 29-35 example 7  US 5 684 057 A (WIERZBICKI RONALD J ET	10-15 1-15
	AL) 4 November 1997 (1997-11-04) cited in the application the whole document	1-13
		·

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

## INTERNATIONAL SEARCH REPORT

information on patent family members

Int al Application No
PCT/US 01/48353

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
US 3640997	A	08-02-1972	US	3763111 A	02-10-1973
US 5030758	Α	09-07-1991	DE	3740634 A1	15-06-1989
			ΑT	107940 T	15-07-1994
			BR	8806304 A	15-08-1989
			CA	1334234 A1	31-01-1995
			DE	3850478 D1	04-08-1994
		<b>V</b>	DK	669188 A	02-06-1989
			EP	0318784 A2	07-06-1989
			ES	2055729 T3	01-09-1994
			FΙ	885532 A ,B,	02-06-1989
			JP	1188525 A	27-07-1989
			JP	2630454 B2	16-07-1997
			KR	136386 B1	25-04-1998
			MX 	13970 A	28-02-1994
US 3941769	A	02-03-1976	DE	2241242 A1	07-03-1974
			AU	5932673 A	20-02-1975
			BE	803782 A1	20-02-1974
			CA	1000698 A1	30-11-1976
			ES	418057 A1	16-03-1976
			FR	2197036 A1	22-03-1974
			GB	1392168 A	30-04-1975
			IT	990377 B	20-06-1975
			JP	1157650 C	25-07-1983
			JP JP	49056909 A 57050811 B	03-06-1974 29-10-1982
			NL.	7311456 A ,B,	26-02-1974
US 5684057		04-11-1997		5648019 A	15-07-1997
03 3004037	~	04 11 1337	US	5547998 A	20-08-1996
			US	5523334 A	04-06-1996
			US	5525641 A	11-06-1996
•			CA	2206551 A1	04-12-1997
			GB	2313838 A	10-12-1997
			ÜS	5677359 A	14-10-1997
			AT	181940 T	15-07-1999
			AU	708710 B2	12-08-1999
			AU	7298396 A	22-05-1997
			BR	9611205 A	30-03-1999
			CA	2182741 A1	02-05-1997
			CN	1201472 A ,B	09-12-1998
			DE	69603198 D1	12-08-1999
			DE	69603198 T2	28-10-1999
			MO	9716477 A1	09-05-1997
			ΕP	0858477 A1	19-08-1998
			ES	2135927 T3	01-11-1999
			NZ	320275 A	29-09-1999
			CA	2182740 A1	02-05-1997
			CA	2182739 A1	02-05-1997